Reactions of Molybdenum Tetrahydrido Complex with Halohydrosilanes

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The thermal reactions of [MoH_4(dppe)$_2$] (**1**, dppe = $Ph_2PCH_2CH_2PPh_2$) with $RSiH_2X$ afford [MoH_2X(dppe)-{[$Ph_2PCH_2CH_2P(Ph)C_6H_4$-*o*]RXSi-*P,P,Si*}] (R = Ph, X = Cl (**5a**); R = *cyclo*-C_6H_{11}, X = Cl (**5b**); and R = Ph, X = Br (**6**)) by activation of the Si–H bond of the silanes and the ortho C–H bond of the phenyl group in the dppe ligand. Reduction of the Si–Cl and Mo–Cl bonds in **5a** with $LiAlH_4$ leads to the formation of the original complex **1** as a result of unusual Si–C bond cleavage. Meanwhile, dehalogenative reduction of **5a** using zinc metal gives the known compound [MoH_3{[$Ph_2PCH_2CH_2P(Ph)C_6H_4$-*o*]$_2$(Ph)Si-*P,P,P,P,Si*}] (**2**). The experimental results reported herein provide certain evidence for the involvement of the silylene species in the unusual formation of the present polydentate phosphinoalkyl–silyl ligands.

Transition-metal silyl complexes constitute a widely studied class of organometallic compounds.[1] Recently, we have reported that the thermal reaction of [MoH_4(dppe)$_2$] (**1**, dppe = $Ph_2PCH_2CH_2PPh_2$) with phenylsilane leads not only to oxidative addition of a Si–H bond to the metal center but also to activation of the ortho C–H bonds of the phenyl groups in the two dppe ligands to give a new class of molybdenum–silyl hydrido complex **2** with a novel pentadentate ligand comprised of a P–P–Si–P–P framework (Scheme 1).[2] We have found that this reaction is not limited to primary silanes. Even in the case of a secondary silane system, similar activation of the Si–H bond and the ortho C–H bond took place to give a hydrido complex **3** with a tridentate ligand comprised of a P–P–Si framework.

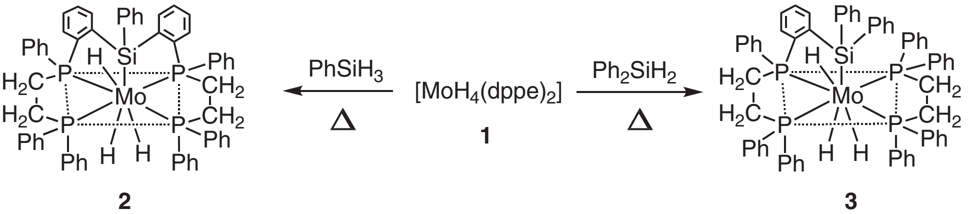
The most plausible pathway for these novel transformations seemed to involve orthometallation by dppe of 16-electron [MoH_2(dppe)$_2$] formed by H_2 loss, followed by oxidative addition of the silanes.[2c] However, significant insight into the mechanism of this unusual C–Si bond formation was obtained by investigation using deuterium-labeling, which suggests that the reaction path includes the intermediacy of a silylene metal complex via an α-migration of hydrogen as is mentioned in the latter part.[2d]

We have also demonstrated the high reactivity of the resulting complexes **2** and **3** toward various substances. To date, we have prepared and structurally characterized a number of new related compounds having these novel polydentate phosphinoalkyl–silyl ligands.[3]

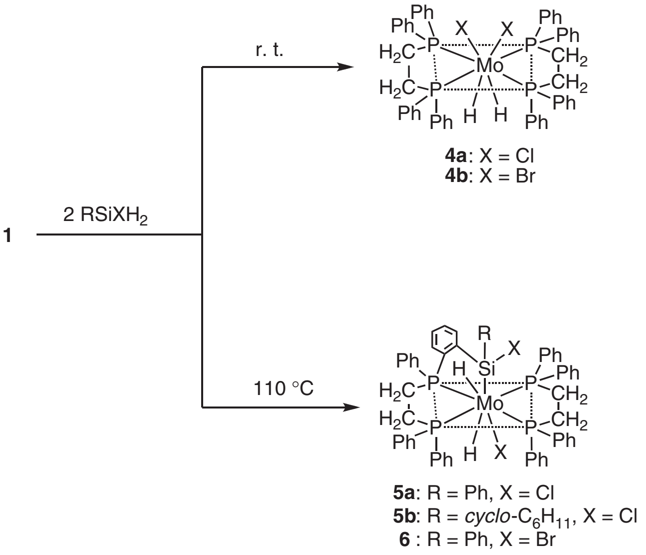
We are particularly interested in exploring how variation of the substituents on the silane affects the formation of the products. Reported here are the results of studies extending this chemistry to halohydrosilanes. It has been established that activation of Si–H bonds in halohydrosilanes would be preferable to that of the Si–X (X = halogen) bond.[1a] However, there have been several reports of facile activation of the Si–X bonds.[4] Thus, it is a moot point whether an oxidative addition of Si–H bond would take place or whether a Si–X bond cleavage would proceed.

Results and Discussion

Reaction of [MoH_4(dppe)$_2$] with Halohydrosilanes. The reactions of **1** with 2 equiv of $RSiH_2X$ (R = Ph, *cyclo*-C_6H_{11}; X = Cl, Br) in toluene at ambient temperature afforded the known *cis*-[MoH_2X_2(dppe)$_2$] (**4a**, X = Cl; **4b**, X = Br)[5] in moderate yields (ca. 50%). It is well-known that in the presence of halocarbons transition-metal hydrido complexes occasion-



Scheme 1.



Scheme 2.

ally undergo metathesis to give the corresponding halogeno compounds.[6] Indeed, ^{1}H NMR study revealed that the reaction between **1** and CCl_4 produced **4a** in a similar manner. Thus, in the case of $RSiH_2X$, the analogous conversion appeared to take place.

The increase of reaction temperature altered the reaction dramatically. At 110 °C, dihydrido complexes (R = Ph, X = Cl (**5a**); R = *cyclo*-C_6H_{11}, X = Cl (**5b**); and R = Ph, X = Br (**6**)) with a tridentate ligand ([$Ph_2PCH_2CH_2P(Ph)C_6H_4$-*o*]RXSi-*P,P,Si*) comprised of the P–P–Si framework were isolated, according to Scheme 2. As expected, the activation of the Si–H bond in the halohydrosilanes and the ortho C–H bond of the phenyl group in the dppe ligand occurred. We have also confirmed that reaction of **4a** with $PhSiH_2Cl$ at 110 °C does not give **5a**. Consequently, the first step is the thermally induced formation of 16-electron [$MoH_2(dppe)_2$]. These results demonstrate that complex **1** displays a pronounced preference for Si–H oxidative addition over Si–X oxidative addition at elevated temperatures. In addition, just as in the foregoing reactions of the secondary silanes, the process would include the intermediacy of a silylene metal complex via α-migration of hydrogen. Probably the resulting trihydrido complexes further react with the halohydrosilanes to produce the halogeno dihydrido compounds **5** and **6**.

Complexes **5** and **6** have been characterized by IR, and ^{1}H and ^{31}P NMR spectroscopies as well as by a preliminary X-ray crystal structure determinations (**5a** and **6**).[7] The NMR spectroscopic data for **5** and **6** illustrate that two complexes exhibit only slight differences in their chemical shifts and coupling patterns; these results are consistent with the X-ray analysis (vide infra).

The IR spectra of complexes **5** and **6** showed ν(Mo–H) at 1716–1718 cm^{-1}, which are at lower frequency than that of **3** by about 10 cm^{-1}. The ^{1}H NMR spectra of **5** and **6** consist of broad peaks arising from PCH_2CH_2P protons between 2.2 and 2.6 ppm and of broad multiplet signals corresponding to two hydrido protons at around −6 ppm, which are at higher field compared with **2** and **3**. The $^{31}P\{^1H\}$ spectra of complexes **5** and **6** show four multiplet resonances at around 84, 63, 59, and 45 ppm with a 1:1:1:1 peak area ratio. The results indicate the presence of four nonequivalent P nuclei in each complex.

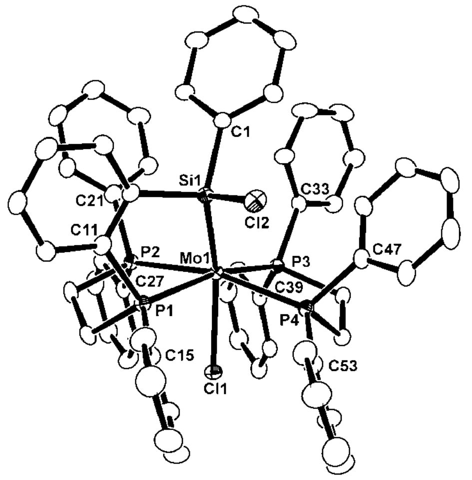
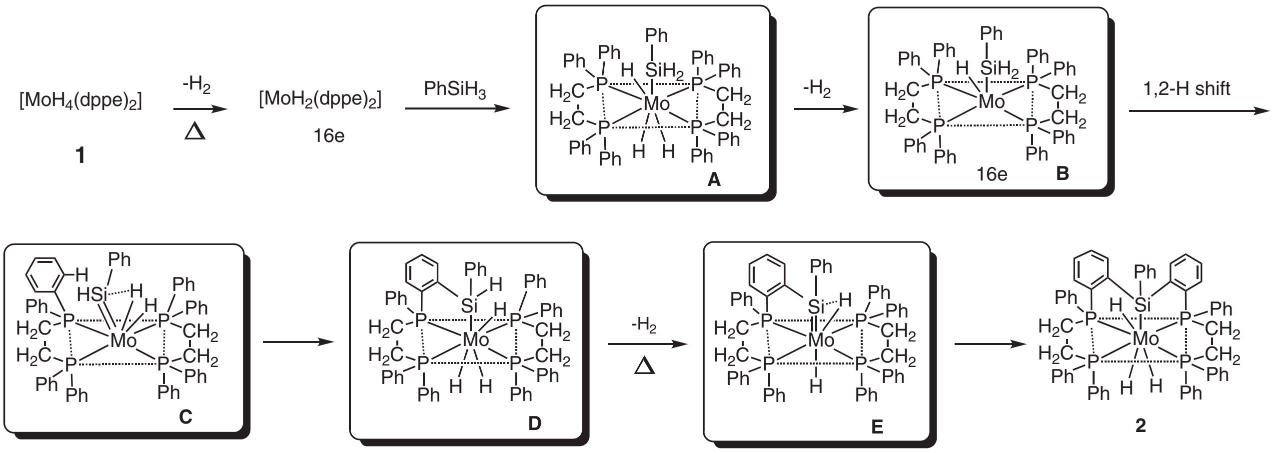


Figure 1. ORTEP drawing of **5a**.

Table 1. Selected Interatomic Distances and Angles in **5a**

Distances/Å			
Mo1–Cl1	2.5421(8)	Mo1–P1	2.4762(9)
Mo1–P2	2.5379(1)	Mo1–P3	2.4819(1)
Mo1–P4	2.5263(1)	Mo1–Si1	2.4744(1)
Cl2–Si1	2.159(2)	Si1–C1	1.904(3)
Si1–C8	1.894(3)		
Angles/°			
Cl1–Mo1–Si1	150.62(4)	P1–Mo1–P2	76.93(3)
P1–Mo1–P3	164.05(3)	P1–Mo1–P4	103.96(4)
P1–Mo1–Si1	74.01(3)	P2–Mo1–P3	96.03(4)
P2–Mo1–Si1	100.25(3)	P3–Mo1–P4	79.10(3)
P3–Mo1–Si1	121.67(3)	P4–Mo1–Si1	94.51(4)
Cl2–Si1–C8	97.92(2)		

Figure 1 shows an ORTEP drawing of **5a**. Some pertinent bond distances and angles are collected in Table 1. The crystal structure unambiguously indicates that the compound contains a new bond between the silicon atom and the ortho carbon of the phenyl group in one of the dppe ligands. Complex **5a** adopts a distorted, square antiprismatic geometry about the molybdenum center; the four phosphorus atoms occupy the equatorial coordination sites. Although the overall geometry of **5a** is very similar to that observed for **3**, the metric parameters differ from one another (vide infra). The chloro ligand is axially coordinated trans to the silyl group. The hydrido ligands are not located. However their presence is confirmed by means of ^{1}H NMR and IR spectroscopy. A conspicuous structural feature is that the Mo–Cl bond of 2.5421(8) Å in **5a** is considerably longer than the value of 2.387 Å in **4a**.[5b] Consequently, the differing trans influence of the hydrido versus silyl ligand is at least semiquantitatively observed. Although both hydrido and silyl groups are known to have good σ-donor ability which is closely concerned with the trans-influence,[8] our results have clearly verified that the silyl group has a high trans-influence much greater than the hydrido ligand.



Scheme 3.

The mean Mo–P bond distance at 2.5056 Å in **5a** is appreciably longer than that of 2.4645 Å in **3**. In contrast the Mo–Si bond length of 2.4744(1) Å in **5a** is significantly shorter than the value of 2.541(2) Å in **3**. This distance is also quite short when compared to the other Mo–Si distances of structurally characterized complexes derived from **2** and **3**, which range from 2.518 to 2.559 Å.[3] Furthermore, the Si–Cl length of 2.159(2) Å in **5a** is considerably longer than the value of 2.079 Å found in Ph_3SiCl.[9] These structural data for **5a** may be understood in terms of an interaction of the anti-bonding σ^*-orbital of silicon to chloride and the molybdenum dπ orbital.[1a]

As mentioned previously, on the basis of deuterium-labeling, we proposed that the reaction between **1** and phenylsilane occurs by the sequence of events shown in Scheme 3.[2d] The first step, the loss of H_2 upon thermolysis of **1** is well documented.[10] The silane addition product **A** would undergo further loss of H_2 to give a putative 16-electron intermediate **B** which rearranges to a hydrido(hydrosilylene) complex **C** via an overall 1,2-H shift. Recently, this type of transformation has been firmly established by Tobita et al. for group 6 transition-metal hydridos $[Cp'(CO)_2(H)W{=}Si(H)\{C(SiMe_3)_3\}]$ ($Cp' = Cp^*$ or η^5-C_5Me_4Et).[11] Strong interactions between the silylene and hydrido ligands have been shown to exist in these complexes, thus the driving force for the formation of **C** may be a similar interligand interaction. The following ortho C–H bond scission of a phenyl group in one of the dppe ligand would produce the presumed intermediate **D**. A similar process (activation of an intramolecular aromatic C–H bond by silylene complexes) has been observed in ruthenium systems.[12] Since we could not detect the silylene intermediate **C** spectroscopically it is assumed that the lifetime of this species might be so short that it would not exist in sufficient concentration to be observable in a ^{1}H NMR spectrum. We think that the present insertion process is very rapid and is promoted by steric acceleration due to easy access of the C–H bond to the active site. The sequence of processes would repeat to attach Si to the other dppe ligand affording the final product **2**.

We have thought that complex **5a** provides a direct approach to verify the validity of the above assumptions. At first glance the intermediate **D** would appear to be accessible through reduction of **5a** with a hydride reagent. Alternatively, dehalogenation of **5a** would lead to the generation of the silylene species **E**. Thus, further study of **5a** was directed toward understanding the reaction chemistry of the chloro substituents on the silyl group and the molybdenum center with the goal of obtaining the mechanistic insight.

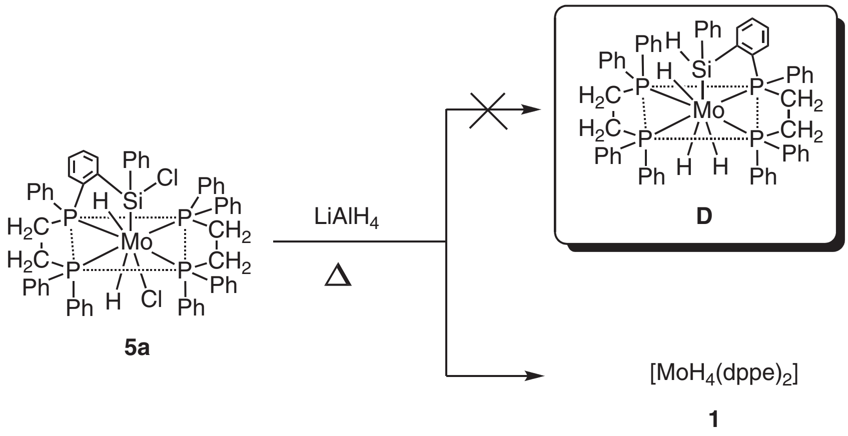
Reduction of 5a with $LiAlH_4$ and Zinc. First we carried out reduction of **5a** with $LiAlH_4$ in THF at 67 °C (Scheme 4). Surprisingly, the ^{1}H NMR spectrum of the crude reaction mixture indicated the major species present to be the original complex **1** (40%). The reaction probably led first to reduction of the Cl groups and then to the Si–Mo and Si–Ph bond cleavage.

An activation of Si–C bonds is potentially important in the development of new processes in organosilicon chemistry, although cleavage of an Si–Ph bond has fewer precedents.[13] It is generally recognized that transition-metal silyl complexes are susceptible to nucleophilic attack at silicon.[1a] In some silyl complexes, $LiAlH_4$ can displace the silyl group as the corresponding silane by direct attack at silicon.[14] However, the cleavage of an alkyl–silicon bond has seldom been observed in these reductions. The formation of **1** is thus highly puzzling at present, and the mechanistic details will be clarified by further work.

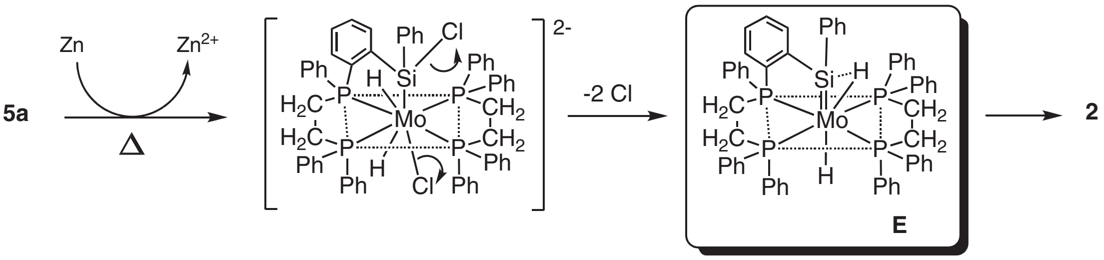
Next we explored the dehalogenation reaction of **5a**. Stirring **5a** in THF with an excess of zinc metal at reflux temperature for 4 h resulted in the formation of a yellow-green solution, from which the anticipated product **2** was isolated as the only major product (27%).[15] The formation of **2** can be rationalized according to Scheme 5. Complex **5a** would undergo a two-electron reduction by Zn metal to form a dianionic species. Subsequent elimination of two chloride anions would yield the silylene species **E** which then inserts into the ortho C–H bond of the phenyl group to give **2**.

Conclusion

The reactions of $[MoH_4(dppe)_2]$ (**1**) with $RSiH_2X$ were investigated. At ambient condition the reactions afford the known *cis*-$[MoH_2X_2(dppe)_2]$; thus, facile activation of the Si–X bonds takes place. On the other hand, the reactions in refluxing toluene lead to the isolation of $[MoH_2X(dppe)\{[Ph_2PCH_2CH_2P(Ph)C_6H_4\text{-}o]RXSi\text{-}P,P,Si\}]$ (R = Ph, X = Cl (**5a**); R = *cyclo*-C_6H_{11}, X = Cl (**5b**); and R = Ph, X = Br (**6**)) with the tridentate phosphinoalkyl–silyl ligand. These reactions proceed



Scheme 4.



Scheme 5.

by a route entirely similar to those reported for complexes **2** and **3**; that is, Si–H, C–H, Si–C, and H–H bond cleavage/formation all occur in the same system. The existence in the resulting complexes of halide substituents seems to make them susceptible to further transformation. Reduction of **5a** with $LiAlH_4$ unexpectedly leads to the formation of the parent complex **1**, which would involve an unusual activation of Si–C bond. In contrast, dehalogenation of **5a** using zinc metal gives complex **2**. The experimental results reported herein provide certain evidence for the involvement of the silylene species in the unusual formation of the present polydentate phosphinoalkyl–silyl ligands. Further studies on these and other related reactions are in progress.

Experimental

General Procedures. All manipulations were performed using standard Schlenk techniques under purified argon. All reagents were purchased from commercial suppliers and used as received without further purification. All solvents were dried by standard methods and were stored under argon. Complex **1**[16] and $RSiH_2X$[17] were synthesized according to procedures previously reported. All NMR spectra were recorded on a JEOL-JNM-270 spectrometer. $^{31}P\{^1H\}$ NMR peak positions were referenced to external PPh_3.

Reactions of 1 with $PhSiH_2X$ at Ambient Temperature. A solution of **1** (0.31 g, 0.35 mmol) and $PhSiH_2Cl$ (100 µL, 0.75 mmol) in benzene (35 mL) was stirred overnight, during which time the solution turned from yellow to orange. The reaction mixture was then allowed to stand for 12 h at 0 °C, whereupon precipitates of unreacted **1** separated. The supernatant solution was removed with a bridge filter. The volatiles were removed in vacuo and the residue thus obtained was washed with diethyl ether (8 mL × 3). The resulting yellowish solid was dried under vacuum to yield 0.27 g (81%) of **4a**. The spectroscopic properties of **4a** are consistent with those of *cis*-$[MoH_2Cl_2(dppe)_2]$.[5] Complex **4b** was prepared in a manner similar to that for **4a** in 85% yield.

Reactions of 1 with $PhSiH_2Cl$ at 110 °C. A solution of **1** (0.28 g, 0.31 mmol) and $PhSiH_2Cl$ (90 µL, 0.63 mmol) in toluene (30 mL) was heated with stirring at 110 °C for 3 h. The resulting solution was concentrated to a volume of 25 mL under reduced pressure. Hexane (3 mL) was then added, and the mixture was allowed to stand for 12 h at 0 °C, whereupon yellow precipitates separated. The product was collected by filtration, washed with hexane (10 mL × 3), and then dried in vacuo to give **5a** (0.23 g, 69%). **5a**: IR data (KBr): ν(Mo–H) 1716 cm^{-1}. ^1H NMR (270 MHz, C_6D_6, ppm): 8.0–6.5 (m, aromatics), 2.6–2.2 (m, PCH_2), −5.80–−6.35 (br m, 2H, Mo*H*). ^{31}P NMR (C_6D_6, ppm): 83.0 (ddd, 1P, $J_{pp} = 5, 21, 121$ Hz), 63.0 (ddd, 1P, $J_{pp} = 10, 21, 116$ Hz), 62.0 (ddd, 1P, $J_{pp} = 10, 27, 121$ Hz), 43.0 (ddd, 1P, $J_{pp} = 5, 27, 116$ Hz). Anal. Calcd for $C_{58}H_{54}Cl_2MoP_4Si$: C, 65.11; H, 5.09%. Found: C, 64.33; H, 5.54%. Complex **5b** was prepared in a manner similar to that for **5a** in 74% yield. **5b**: IR data (KBr): ν(Mo–H) 1718 cm^{-1}. ^1H NMR (270 MHz, C_6D_6, ppm): 8.0–6.5 (m, aromatics), 2.6–2.2 (m, PCH_2), 2.0–1.2 (m, 11H, C_6H_{11}), −5.80–−6.75 (br m, 2H, Mo*H*). ^{31}P NMR (C_6D_6, ppm): 85.0 (ddd, 1P, $J_{pp} = 5, 22, 118$ Hz), 61.0 (ddd, 1P, $J_{pp} = 8, 22, 115$ Hz), 57.0 (ddd, 1P, $J_{pp} = 8, 27, 118$ Hz), 46.0 (ddd, 1P, $J_{pp} = 5, 27, 115$ Hz). Anal. Calcd for $C_{58}H_{60}Cl_2MoP_4Si$: C, 64.75; H, 5.62%. Found: C, 64.62; H, 5.96%.

Reactions of 1 with $PhSiH_2Br$ at 110 °C. $PhSiH_2Br$ (110 µL, 0.59 mmol) was added dropwise with stirring to a solution of **1** (0.27 g, 0.30 mmol) in toluene (30 mL) at 110 °C. After stirring for 3 h the resulting solution was concentrated to a volume of 25 mL under reduced pressure. Hexane (2 mL) was then added, and the mixture was allowed to stand for 12 h at 0 °C, whereupon yellow precipitates separated. The product was collected by filtration, washed with hexane (10 mL × 3), and then dried in vacuo to give **6** (0.28 g, 80%). **6**: IR data (KBr): ν(Mo–H) 1716 cm^{-1}. ^{1}H NMR (270 MHz, C_6D_6, ppm): 8.0–6.5 (m, aromatics), 2.6–2.2 (m, PCH_2), −6.25–−6.75 (br m, 2H, MoH). ^{31}P NMR (C_6D_6, ppm): 79.0 (ddd, 1P, $J_{pp} = 5, 22, 116$ Hz), 56.0 (ddd, 1P, $J_{pp} = 12, 27, 116$ Hz), 53.0 (ddd, 1P, $J_{pp} = 12, 22, 112$ Hz), 44.0 (ddd, 1P, $J_{pp} = 5, 27, 112$ Hz). At present, no sample suitable for combustion analysis is available.

Reduction of 5a with LiAlH$_4$. A slurry of **5a** (0.15 g, 0.14 mmol) and $LiAlH_4$ (0.029 g, 0.75 mmol) in THF (10 mL) was prepared at 0 °C and warmed to ambient temperature. The slurry was then allowed to reflux overnight. Subsequently the reaction mixture was cooled to ambient temperature and slowly hydrolyzed with water (1 mL), following which the solvent and volatiles were removed under vacuum. The resulting solid was extracted with benzene. After evaporation of the benzene, the residue was washed with hexane (5 mL × 3) and dried under vacuum, yielding 0.05 g (40%) of **1**.

Reduction of 5a with Zinc. A slurry of **5a** (0.16 g, 0.16 mmol) and zinc powder (0.10 g, 1.6 mmol) in THF (15 mL) was allowed to reflux for 4 h. After removal of ca. 10% of the solvent in vacuo, hexane (5 mL) was added, and the mixture was allowed to stand for 12 h at 0 °C. The resulting mixture was filtered, and the filtrate was evaporated in vacuo. The residue was washed with hexane (5 mL × 3) and dried under vacuum, yielding 0.04 g (27%) of **2**.

X-ray Crystallographic Analysis of 5a. Single crystals of **5a** suitable for X-ray analysis were obtained by slow recrystallization from toluene–hexane. The intensity data were collected on a Rigaku Saturn CCD area detector with graphite monochromated Mo Kα radiation ($\lambda = 0.71070$ Å). The structure was solved by direct methods (SIR2002[18]) and expanded using Fourier techniques (DIRDIF99[19]). Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were refined using the riding model. Crystal data for $\mathbf{5}\cdot C_7H_8$ at −160 °C: $C_{65}H_{60}Cl_2MoP_4Si$, MW = 1160.02, triclinic, space group $P\bar{1}$ (#2), $Z = 2$, $a = 12.7418(1)$ Å, $b = 13.4611(1)$ Å, $c = 20.5471(2)$ Å, $\alpha = 72.698(5)°$, $\beta = 75.800(6)°$, $\gamma = 62.325(4)°$, $V = 2955.8(4)$ Å^3, $D_{calcd} = 1.303$ g cm^{-3}, $2\theta_{max} = 55.0°$, $R1$ ($I > 2\sigma(I)$) = 0.0520, $wR2$ ($I > 2\sigma(I)$) = 0.2062 for 10087 reflections and 718 parameters, GOF = 1.610.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-750467. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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7 We have confirmed that the molecular structure of **6** is analogous to that of **5a**. The crystallographic details of **6** will be discussed elsewhere.

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